

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Improvements in or relating to Thermo-couples made with Thermo-electric Alloys

- We, AKTIEBOLAGET KANTHAL, of Hallstahammar, Sweden, a corporation duly organized and existing under the laws of the Kingdom of Sweden, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to a thermo-couple, one leg of which is formed from a thermo-electric alloy which is particularly suitable for use at very elevated temperatures, and which consists of an intermetallic composition containing molybdenum, silicon and aluminium.
- It is known (J. Appl. Phys. 1953) that MoSi_2 exhibits a thermo-electric effect within the range from -60°C . to $+600^\circ \text{C}$., with respect to platinum, which nearly corresponds to that of copper. It is therefore known to use the highly temperature-resistant molybdenum disilicide as a thermo-couple. It is also known (British Patent Specification No. 739,693) that molybdenum disilicide with 30—40% of Si and certain other constituents may be used in thermo-couples at elevated temperatures. The suggested other constituents are titanium silicide, tungsten silicide, chromium silicide, aluminium oxide, thorium oxide, titanium oxide, zirconium oxide, and silicon carbide. Furthermore, it is known that up to 25% of the silicon atoms of the molybdenum disilicide may be substituted by carbon, boron or nitrogen.
- The thermo-electric alloy forming the positive leg of the thermo-couple of the present invention is distinguished from such previously used alloys in that it is a molybdenum disilicide alloy, wherein 20—60 percent of the silicon atoms have been substituted by atoms of aluminium. The crystal structure of the molybdenum disilicide, which is normally of the C 11 lattice type, becomes entirely converted into the C 40 lattice or chromium silicide type. This modification of the crystal structure surprisingly results in the production of a considerable thermo-electric effect by the alloy used according to the present invention, as compared with pure MoSi_2 , for example. Other advantages are high mechanical strength, oxidation resistance and resistance to thermal shocks. By variation of the Al-content, variations in the thermo-electric effect may be obtained which are not necessarily accompanied by serious deterioration of the mechanical or chemical properties. In this respect, the alloys according to the present invention are distinguished from the previously known thermo-electric molybdenum silicide base alloys. A thermo-couple according to the invention, which is suitable for use at elevated temperatures in oxidising atmospheres, thus comprises at least one leg which contains a thermo-electric alloy as described above. Preferably, such a thermo-couple has a positive leg containing the said alloy, and a negative leg containing molybdenum disilicide.
- An alloy is described in British Patent Specification No. 731,616 for use as a high temperature electrical resistance, which has the weight composition; molybdenum 50—84%, silicon 15—48%, and aluminium 1—35%. This alloy has not hitherto been known to have any thermoelectric properties, however.
- The thermo-electric alloy used according to the invention may also, if desired, include one or more other metals, in which case up to a maximum of 50 per cent of the molybdenum atoms are substituted by atoms of one or more of the metals Ti, Zr, Hf, Ta, Nb, V, W and Cr. Thus, the composition of these thermo-electric alloys may be written:—

[Price 4s. 6d.]

Price 25p

($\text{Mo}_{1-y}\text{M}_y$) ($\text{Si}_{1-x}\text{Al}_x$)₂, wherein $0.2 < x < 0.6$ and $0 < y < 0.5$ and M is one or more of the other metals specified.

5 The legs containing the thermo-electric alloy of thermo-couples according to the invention are preferably made by a powder metallurgy process by sintering after admixture of a ceramic binding substance. Preferably, the ceramic binding substance is composed essentially of very finely powdered silica, preferably in the form of a glass. However, it may also contain other oxides or silicon carbide. Conveniently, the final sintering is carried out in air, in which case a certain internal oxidation takes place. The ceramic component should preferably not exceed 30 percent by weight of the material.

20 Thermo-couples according to the invention may also advantageously be used as heating resistors for producing high temperatures. In such a case, the element is coupled to serve as thermo-couple only for the short periods when the thermo-voltage is measured and to serve as an electrical heating resistor for the remaining periods. The resulting thermo-voltage may be used in practice for controlling the current supply to the resistor through a relay. Preferably, the welded joint between the two legs should be disposed internally of the furnace, at or adjacent a lead-in electrode, so that it is not subjected to higher temperatures than those of the furnace room.

35 The following example illustrates a practical embodiment of a thermo-couple according to the invention for use at 1600° or 1700° C:—

Positive leg: 4% by weight SiO_2
96% by weight alloy of the following composition ($\text{Mo}_{0.7}\text{Ti}_{0.3}$) ($\text{Si}_{0.5}\text{Al}_{0.5}$)₂

Negative leg: 9% by weight SiO_2
91% by weight MoSi_2

45 The thermo-electric effect increased regularly with the temperature and attained the following values:—

800° C.	10 millivolts
1000° C.	14 "
1200° C.	19 "
1400° C.	24 "
1600° C.	31 "

50 Both legs were 6 mm cylindrical rods, made by extrusion and sintering, and joined by resistance butt welding. The more oxidation-resistant negative leg may alternatively be formed as a tube which is closed at one end and surrounds the rod-shaped positive leg.

55 The above disclosed combination may also be used as an electrical heating resistor and should then have the following dimensions: 60 The positive leg is formed as a hair pin,

whereof one portion is of 6 mm diameter and acts as glowing zone. One end of the loop is enlarged to 14 mm and is long enough to extend out from the furnace as a cold lead-in electrode. The other end is welded to a 9 mm negative leg which is similarly elongated to act as a cold lead-in electrode. As the alloy forming the negative leg has about half as high a specific resistance at 1600° C. as the alloy forming the positive leg, this lead-in electrode remains cool enough without special cooling devices. For the same reason, the welded joint attains the same temperature as the furnace room, provided it is disposed at a suitable place in the furnace, notwithstanding the fact that it is disposed adjacent the hot glowing zone.

WHAT WE CLAIM IS:—

1. A thermo-couple which is suitable for use at elevated temperatures in oxidizing atmospheres, having at least one leg which comprises a thermo-electric molybdenum disilicide alloy having the crystal structure C 40 (CrSi_2 -type) in which 20—60 percent of the silicon atoms have been substituted by aluminium atoms.

2. A thermo-couple according to Claim 1, having a positive leg containing the thermo-electric alloy, and a negative leg containing molybdenum disilicide.

3. A thermo-couple as claimed in Claim 1 or 2, in which the thermo-electric alloy is of the composition ($\text{Mo}_{1-y}\text{M}_y$) ($\text{Si}_{1-x}\text{Al}_x$)₂, wherein M is one or more of the metals Ti, Zr, Hf, Nb, Ta, V, W, Cr, x is between 0.2 and 0.6 and y is between 0 and 0.5.

4. A thermo-couple as claimed in Claim 3, in which the alloy has the composition ($\text{Mo}_{0.7}\text{Ti}_{0.3}$) ($\text{Si}_{0.5}\text{Al}_{0.5}$)₂.

5. A thermo-couple as claimed in any preceding claim, in which the thermo-electric alloy is in powder form sintered in the presence of a ceramic binding agent.

6. A thermo-couple as claimed in Claim 5, in which the binding agent comprises not more than 30% of the material constituting the leg.

7. A thermo-couple as claimed in Claim 5 or 6, in which the binding agent comprises finely-divided silica.

8. A thermo-couple as claimed in Claim 7, in which the binding agent is a glass.

9. A thermo-couple according to Claim 1, substantially as hereinbefore described.

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